Ionophoretic Study of Bivalent Metal - Succinate Complexes

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Ionophoretic technique has been used for the study of Cu^{2+} and Co^{2+} by measuring decrease in the concentration of metal ion in anodic compartment. The value of stability constant of different species are found to be: $CuHL^+$ (log K = 2.12), CuL (log K = 2.56) and $CoHL^+$ (log K = 1.97) at 30° C and μ = 0.1.

Migration of ions of pure electrolyte solution has been widely studied. This paper deals with migration in mixed electrolyte solution to assess the stability constants of different species formed in metal succinate solutions.

EXPERIMENTAL

Details of electrophoretic tube and procedure are described earlier [1]. The tube is 18.0 cm long and of 5 mm bore with a stopper in the middle and is fused perpendicularly at the ends with short wider tubes of 1.2 cm bore. 10 ml of aliquot of ionophoretic solution is taken in this tube and then thermostated at 30° C. The position of the tube is adjusted in such a way that the level of the solution in one wide end arm reaches a circular mark on it. This adjustment fixes the volumes of the solution on both sides of the middle stopper. Two 0.5x0.5 cm^2 platinum electrodes are dipped (one in each arm) and a potential difference at 50 V is applied between them. Electrolysis of the solution is allowed for 45 minutes; after this the middle stopper of the tube is closed. The solution of the anodic compartment is taken out in a 10 ml flask. Metal ion content in this is determined colorimetrically.

Theoretical Considerations

As mentioned earlier [1], the overall mobility is a composite parameter contributed by different ionic species of the metal ion uncomplexed, 1:1 complex and 1:2 complex etc. When three species are present in the solutions, the concentration of different species can be written as:

Free metal ion concentration =

$$\frac{1}{1 + K_1[L] + K_1 K_2[L]^2}$$

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1:1 metal complex concentration =

$$\frac{K_1[L]^2}{1 + K_1[L] + K_1 K_2[L]^2}$$

1:2 metal complex concentration =

$$\frac{K_1 K_2[L]^2}{1 + K_1[L] + K_1 K_2[L]^2}$$

and the overall mobility is given by

$$u = \frac{u_0 + u_1 K_1[L] + u_2 K_1 K_2[L]^2}{1 + K_1[L] + K_1 K_2[L]^2}$$

In the region between the first and second plateau, the system contains overwhelmingly a mixture of free metal and 1:1 complex. The existance of 1:2 complex can be neglected in this region and hence the third term in both numerator and denominator of the expression of u can justifiably neglected. By substituting $K_1[L] = 1$, u reduces to $(u_0 + u_1) / 2$ or in this region $K_1 = 1/[L]$.

RESULTS

A set of solutions containing 5.0×10^{-4} M Cu^{2+}, 0.1 M $HClO_4$ and 2.0×10^{-2} M Succinic acid at different pHs (by adding NaOH solution) was prepared. The copper content of the solution was converted into copper thiocyanate complex. The volume was made up to the mark in the flask and then absorbance at λ =408 nm was measured with Spekol Spectrocolorimeter [2].

For the study of Co^{2+} - succinate system 5.0×10^{-4} M Co^{2+} was used while other ingrediants remained same as in Cu-Succinic acid system. After electrolysis, the cobalt content in the anodic compartment was determined colorimetrically at λ = 625 nm by converting it into cobalt thiocyanate [2] complex. It was found that Cu^{2+} thiocynate and Co^{2+} thiocyanate complexes obey Beer's law in presence of Succinic acid.

Fig. 1 Mobility curve [Co(II) - succinic acid system] •[Cu(II) - succinic acid system] (Temp. 30°C, Ionic strength = 0.1)

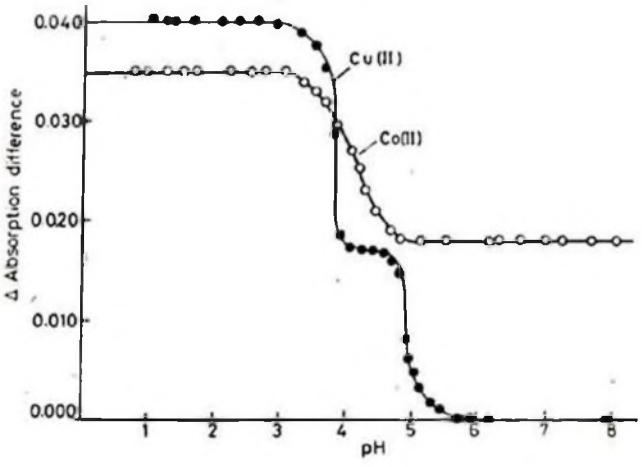


Fig.1 shows graphical representation of difference in absorbance due to metal ion present in the anodic compartment before and after electrolysis as a function of pH of the reaction mixtures. The difference is due to the metal ion lost by Ionophoretic mobility. Thus the figure gives the change of overall mobility of

the metal species with change in hydrogen ion in the reaction mixtures. In case of Cu^{2+} ion there are three plateaus whereas in two plateaus in Co^{2+} ion. The first plateau at low pH corresponds to the region where metal ion is uncomplexed. Further increase in pH brings about a progressive decrease in overall ionic mobility showing complexation with the mononegative succinate anion. This decrease continues till it reaches a second plateau still of positive mobility. Beyond this plateau, further increase of pH in case of copper solution results in a second decrease till a third plateau of zero mobility. This is due to the 1:1 complex species of divalent metal ion and the normal succinate ion, but there is no decrease in mobility in case of cobalt.

From the graph, the point where $u = u_0 + u_1) / 2$ can be marked and the value of pH can be read out. The concentration of the ligand (mononegative succinate anion) is calculated using the pK value of the succinic acid ($\log K_1 = 5.24$). The reciprocal of this gives the stability constant of the 1:1 complex. Considering the region between the second and the third plateau and the pK_2 of succinic acid ($\log K_2 = 4.00$) the stability constant of the 1:2 complex is calculated similarly.

The calculated stability constants of the succinate complexes in case of Cu^{2+} and Co^{2+} are elucidated in the Table 1.

Beyond the second plateau, further increase in pH does not change the path of the curve ruling out any possiblity of formation of hydroxy complex.

Table 1

Stability Constant of Succinato Complexes

Temp = 30° C, ionic strength = 0.1

Metal ion	$\log K^{M}_{MIIL}$	$\log K^{MIIL}_{ML2}$
Cu(II)	2.12	2.56
literature (at 25° C)		2.60 [5]
Co(II)	1.97	
literature (at 20° C)	0.99 [5]	

It is to be noted that the method undertaken in this paper is novel. The actual purpose is to find out that it is suitable for the study of stability constants. It can be seen that our values are in fair agreement with the literature values; the small variation can be attributed to the temperature difference and the condition of working and mode of calculation.

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